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# Dispersion relations and lattice dynamics of diphenylalanine nanotubes

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**Abstract.** In this work we demonstrate the structural similarity between nanotubes of dipeptide diphenylalanine and one-dimensional locally resonant metamaterials. We developed dynamical model of nanotubes, derived corresponding dispersion relations, and analyzed the origin of the behavior of their optical branch leading to band gap formation. We demonstrate also that the width of the band gap can be varied by tuning the interaction between core molecules. Obtained results are general for many locally resonant metamaterials.

## 1. Introduction

Acoustic metamaterials are defined as artificial solids composed of meta-atoms with specific interaction with acoustic waves [1,2] endowing bulk material with unconventional effective properties such as acoustic band structure [2,3], negative refraction [2, 4], negative elastic modulus [5,6], and negative mass density [2, 7]. Such metamaterials can be used for transformation of acoustic waves and cloaking objects [1,8], for realizing unidirectional transmission in acoustic and thermal diodes [8], for acoustic imaging beyond the diffraction limit [1] etc.

Bioorganic materials acquiring multilevel hierarchical structure in the result of self-assembly processes are recognized nowadays as advanced materials for manufacturing various functional micro- and nanodevices [9]. The nanotubes of the simplest aromatic dipeptide diphenylalanine (D-Phe-D-Phe, FF) has recently attracted attention of researchers due to its pronounced piezoelectric [10,11], ferroelectric [12,13], pyroelectric [14] and elastic [15] properties. A lot of new biocompatible microelectronic and micromechanical devices based on FF nanotubes have been suggested [10,16,17].

In this work we consider lattice dynamics of diphenylalanine nanotubes. We developed simple dynamical model of such nanotubes, which is quite similar to that used for description of one-dimensional (1D) locally resonant metamaterials. We derived corresponding dispersion relations and revealed the origin of a non-typical behavior of their optical branch leading to band gap formation. We demonstrate also the way for tuning the width of the band gap.

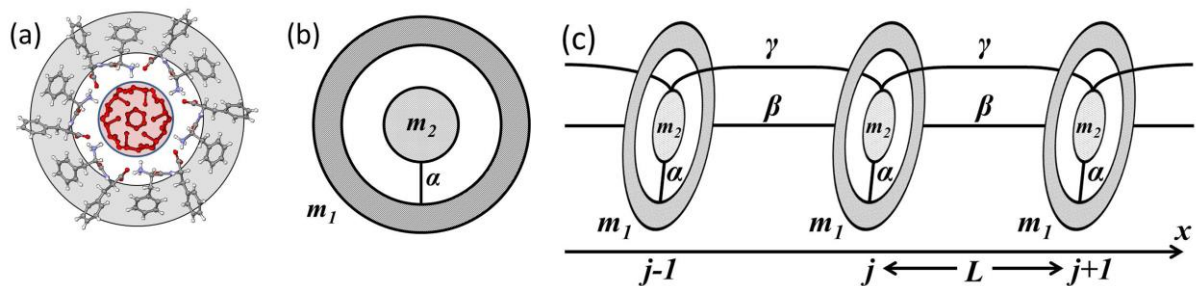
## 2. Model description

A simple 1D dynamical model of FF nanotubes considers a helical FF nanotube as a linear chain of mass-in-mass units equivalent to the nanotube's unit cell [18]. The unit cell of the nanotube consists of two interacting subsystems: FF ring (6 monomers) and water core (24 molecules, 4 molecules per FF monomer [19]) inside the ring (Fig. 1(a)). Water molecules are held in the nanochannel core by



radially oriented hydrogen bonds with FF monomers, whereas the latter interact among themselves via both hydrogen bonds and van der Waals forces [20,21]. Interaction between the FF ring and the water subsystem for transversal  $a$  and  $b$  directions is characterized by the same effective spring constant  $\alpha$ . Longitudinal interaction between adjacent rings and water therein occurs with effective spring constants  $\beta$  and  $\gamma$ , respectively. Individual nanotubes bond together by aromatic rings and form microtubes, which can be considered as a hexagonal crystal [21,22].

This model was successively used recently for determination the origin of high rigidity of FF nanotubes [18] and for description of high temperature phase transitions [23]. It is worth noting that suggested model is similar to that used for description of acoustic metamaterials consisting of chains of local resonators [3,6]. Such structural similarity allows expecting dynamical and elastic properties of FF nanotubes similar to those inherent to such quite exotic metamaterials.



**Figure 1.** Representation of FF nanotube as 1D lattice of interacting mass-in-mass units. (a) Typical unit cell of FF nanotube; (b) its mass-in-mass representation; (c) 1D lattice of interacting mass-in-mass units. Solid lines show interactions between masses with spring constants denoted by  $\alpha$ ,  $\beta$  and  $\gamma$ .

### 3. Results and discussion

The equations of motion for suggested dynamical model can be written in the form:

$$\begin{cases} m_1 \frac{d^2 u_1^j}{dt^2} + \alpha(u_1^j - u_2^j) + \beta(2u_1^j - u_1^{j-1} - u_1^{j+1}) = 0 \\ m_2 \frac{d^2 u_2^j}{dt^2} + \alpha(u_2^j - u_1^j) + \gamma(2u_2^j - u_2^{j-1} - u_2^{j+1}) = 0 \end{cases} \quad (1)$$

Here  $u_1^j$  and  $u_2^j$  are displacements of the  $j$ -th FF ring and water core respectively. These equations are similar to those written for local resonance materials [6], but include additional interaction between cores. Solution of Eqs. (1) for  $(j+n)$ -th unit can be found in accordance with conventional calculation method [24] in the form of harmonic plane waves:

$$u_1^{j+n} = B_1 \exp[i(q(x+nL) - \omega t)] \quad \text{and} \quad u_2^{j+n} = B_2 \exp[i(q(x+nL) - \omega t)] \quad (2)$$

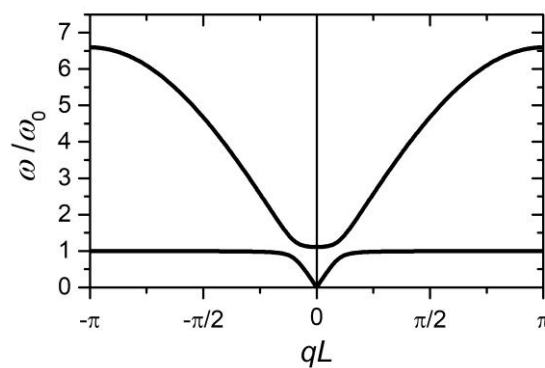
Here  $L$  is a distance between mass-in-mass units equivalent to cell parameter  $c$  of FF nanotube ( $c = 5.46 \text{ \AA}$ ),  $q$  – wavenumber,  $\omega$  – vibration frequency. Substitution of Eqs. (2) into equations of motion (1) and solving the corresponding eigenvalue problem provide the dispersion relations for the system under consideration [18]:

$$\omega^2 = \frac{\alpha}{2} \lambda(qL) \left\{ 1 \pm \sqrt{1 - 4 \frac{f(qL)g(qL) - 1}{\mu M \lambda(qL)^2}} \right\}, \quad (3)$$

where  $\mu^{-1} = m_1^{-1} + m_2^{-1}$  – reduced mass,  $M = m_1 + m_2$  – total mass of the unit cell,  $f(qL) = 1 + 2(\beta/\alpha)[1 - \cos(qL)]$ ,  $g(qL) = 1 + 2(\gamma/\alpha)[1 - \cos(qL)]$  and  $\lambda(qL) = (f(qL)m_2 + g(qL)m_1)/(m_1 m_2)$ .

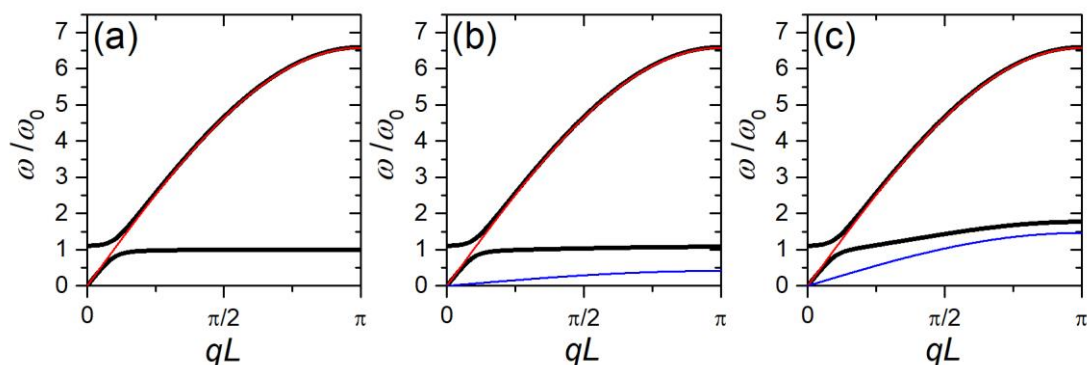
Numerical values of parameters used in Eq. (3) can be found from literature data. The masses of FF ring and water core are:  $m_1 = 3.11 \times 10^{-24}$  kg and  $m_2 = 0.72 \times 10^{-24}$  kg [18]. Spring constants  $\alpha$  and  $\gamma$  can be found by classical formula  $\omega^2 = \alpha/m$ :  $\alpha = 9.34$  N/m (from Raman spectra of FF nanotubes [18]) and  $\gamma = 0.353$  N/m (from frequency of water dimer translation vibrations [25]). Spring constant  $\beta = 438$  N/m can be found by Eq. (3) in Ref. 18 using elastic constant  $C_{33}$  obtained in Ref. 15.

The dispersion relations (3) provide two vibration branches presented in Fig. 2 in the interval  $qL \in [-\pi, \pi]$ . A non-typical curvature of the optical branch (the sign “+” in the Eq. (3)) should be noted. In case of classical crystal with two atoms per primitive cell the frequency of this dispersion branch gradually decreases from the center of the Brillouin zone to its edge [24]. In the present case an opposite behavior is observed. Such behavior was observed earlier for 1D locally resonance metamaterials [6,26], but its origin almost was not discussed.



**Figure 2.** Dispersion curves for the mass-in-mass lattice representing FF nanotube. Vibration frequency  $\omega$  is normalized over  $\omega_0$ , the local resonance frequency of mass-in-mass unit:  $\omega_0^2 = \alpha/m_2$ .

We found that the reason of the observed behavior of the optical branch is interaction (with spring constant  $\alpha$ ) of acoustic vibrations of two chains: (1) a chain consisting of FF rings, and (2) a chain consisting of water cores (Fig. 1c). The optical branch in mass-in-mass model far from the center of Brillouin zone is determined by acoustic vibrations of the first chain of masses  $m_1$  (red lines in Fig. 3). In case of  $\gamma = 0$  (no interaction between water cores) inherent acoustic vibrations of the second chain are absent, and the bottom acoustic branch in mass-in-mass model is formed due to vibrations transmission from first chain to the second. In the vicinity of the Brillouin zone center the interaction between two chains distorts both branches and leads to formation of the phononic band gap.



**Figure 3.** Dispersion curves for different  $\gamma$ : (a)  $\gamma = 0$  N/m, (b)  $\gamma = 0.353$  N/m and (c)  $\gamma = 5$  N/m. Black lines – mass-in-mass model. Red lines – acoustic dispersion branch of a linear chain consisting of masses  $m_1$  only. Blue lines – acoustic dispersion branch of a linear chain consisting of masses  $m_2$  only.

Taking into account an interaction between water cores leads to appearance of another acoustic dispersion branch inherent to the second chain vibrations (blue lines in Figs. 3b,c). In the vicinity of the center of Brillouin zone these vibrations provide negligible effect on the mass-in-mass model, whereas away the center they lead to distortion of the resulted acoustic branch (bottom black curve in Figs. 3b,c) and band gap narrowing. Thus, tuning the interaction between cores (e.g., by the variation of the core molecules) allows control the width of the phononic band gap in FF nanotubes.

#### 4. Conclusions

Finally, in this work we found that lattice dynamics of FF nanotube is quite close to that of locally resonant metamaterials. Derived dispersion relations demonstrate non-typical behavior of optical branch and formation of the band gap. Additional interaction between cores in local resonators, usually excluded from consideration in acoustic metamaterials, provides a tool for variation of the band gap width. Thus, FF nanotubes represent a convenient object for experimental study of various unconventional effects inherent to acoustic metamaterials at the nanoscale level.

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